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(54) Title
 MISCIBLE THERMOPLASTIC COMPOSITIONS CONTAINING POLYAMIDE/AMORPHOUS
 POLYAMIDE BLENDS

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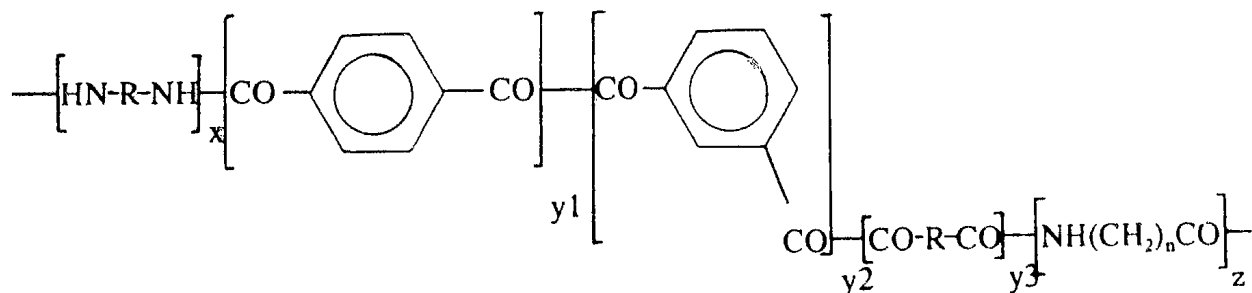
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(56) Prior Art Documents
 AU 59388/90 G08L 77/02
 AU 30473/92 C08L 7706
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(57) Claim

1. A thermoplastic polymeric composition comprising:

- (A) a first polyamide which is one or more aliphatic or cycloaliphatic polyamides; and
 (B) a second amorphous copolyamide which is represented by the following formula:



wherein:

$$x + y1 + y2 + y3 + z = 1$$

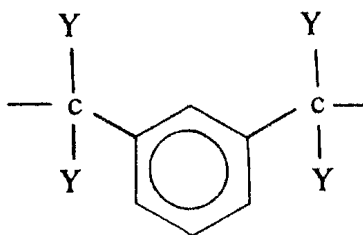
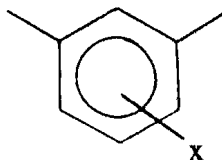
and,

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$$y_1 + y_2 + y_3 = x$$

wherein n has a value of 5 - 11, and z = 0 - 0.5 and wherein R may be selected from the group consisting of :



wherein x is selected from the group consisting of $-\text{CH}_3$ -, an n-alkyl group, and halides, Y is selected from the group consisting of H and $-\text{CH}_3$ -, and R^1 is an α,ω -alkylene radical containing 4 to 18 carbon atoms wherein (A) and (B) are substantially miscible when formed into a blend composition.



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<p>(21) International Application Number: PCT US93/03093 (22) International Filing Date: 1 April 1993 (01.04.93) (30) Priority data: 868.602 14 April 1992 (14.04.92) US (71) Applicant: ALLIED-SIGNAL INC. [US US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). (72) Inventors: AKKAPEDDI, Murali, Krishna ; 7 Manor Drive, Morristown, NJ 07960 (US). GLANS, Jeffrey, Harper ; 20 Washington Avenue, Morristown, NJ 07960 (US). PARMER, Jerome, Forest ; 110 South Louis Street, Mt. Prospect, IL 60056 (US).</p>		<p>(74) Agent: BUEFKER, Ronald, A., Allied-Signal Inc., 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). (81) Designated States: AU, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SI). Published <i>With international search report.</i></p> <p style="font-size: 2em; text-align: center;">67 1991</p>
<p>(54) Title: MISCIBLE THERMOPLASTIC COMPOSITIONS CONTAINING POLYAMIDE AMORPHOUS POLYAMIDE BLENDS</p>		
<p>(57) Abstract</p> <p>Thermoplastic polymeric compositions which feature good physical properties which are relatively insensitive to humidity and further exhibit good barrier properties of the compositions comprise: (A) a first conventional polyamide, and (B) an amorphous copolyamide which is polymerized from (B₁) a polyamide forming monomer selected from the group consisting of lactams, aminoalkanoic acids and mixture thereof wherein the monomer is present in a molar proportion of between about 0 and 50 %, (B₂) a diamine selected from the group consisting of aralkylene diamines, cycloalkylene diamines and mixtures thereof, the diamine being present in a molar proportion of between about 25 and 60 %, (B₃) a dicarboxylic acid selected from the group of an aromatic dicarboxylic acid, aralkylene dicarboxylic acids, and aliphatic dicarboxylic acids; preferably the use of an aliphatic dicarboxylic acid in conjunction with an aromatic dicarboxylic acid is preferred, at least one aromatic diacid, the dicarboxylic acid being present in a molar proportion of between about 25 and 60 %, wherein the (A) and (B) are substantially miscible when formed into a blend composition. The blend composition finds use as a molding composition, as well as a film forming composition, alternatively, may be formed into a variety of articles which exhibit improved physical properties.</p>		

MISCIBLE THERMOPLASTIC COMPOSITIONS CONTAINING
POLYAMIDE/AMORPHOUS POLYAMIDE BLENDS

BACKGROUND

5 1. Field of the Invention

The present invention relates to thermoplastic polymeric molding compositions; more particularly the present invention is related to miscible thermoplastic polymeric blend compositions comprising at least one
10 polyamide, and at least one amorphous polyamide composition wherein the molding composition may be characterized as having good gas barrier properties, and/or good physical strength characteristics, even under conditions of high humidity.

15

2. Description of the Prior Art

As is known, there are exant a multitude of moldable thermoplastic compositions which comprise a polyamide. Polyamides are desirable engineering
20 materials due to their excellent strength characteristics including impact strength and wear resistance which results from high crystallinity of such materials. They are readily processable and formable into a variety of articles and shapes, and
25 which are readily available. However, polyamides are also known to the art to be particularly sensitive to moisture absorption, such as might be occasioned during use in humid conditions or wherein an article is contacted with water, as a consequence of which
30 appreciable degradation of many desirable physical properties of the polyamide are known to result. Further, polyamides are known to exhibit poor vapor

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barrier properties to such gases as oxygen, and of course, water vapor.

In order to overcome these shortcomings, the prior art is replete with improved moldable thermoplastic
5 compositions which suggest a broad range of additional constituents which may be used in conjunction with a polyamide in order to achieve selected improvements in such compositions.

U.S. Patent 4,952,628 to Blatz describes
10 thermoplastic blend materials comprising an essentially of about 50 - 95 weight percent of an amorphous polyamide with about 5 - 50 weight percent of a copolymerized ethylene/vinyl alcohol polymer having an ethylene content of between 0 - 60%. The blend
15 materials taught by Blatz feature physical properties which have a reduced sensitivity to humidity, and improved barrier properties. The blends taught therein provide films and film layers within rigid packaging structures which feature good vapor barrier
20 characteristics.

U.S. Patent 4,983,719 to Fox et al. provides an amorphous polyamide composition which is a reaction product of a paraxylylene diamine, adipic acid and isophthalic acid; the polyamide composition features
25 excellent oxygen barrier characteristics and finds particular use as a container layer in rigid food packaging structures.

U.S. Patent 4,467,011 to Brooks et al. provides injection moldable compositions useful in forming
30 laminates for films and rigid structures which include an amorphous polyamide and polyamide-imide copolymers. The compositions are particularly useful in forming coatings for glass fibers.

U.S. Patents 4,788,248 and 4,788,249 to Maresca et
35 al. provides thermoplastic resin blends which comprise

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a polyamide, a resin which may be a polycarbonate, polyester carbonate, or polyarylate, a compatibilizing copolymer of polyamide-polyester, and optionally a rubbery impact modifier. The compositions may include
5 an amorphous polyamide which is derived from hexamethylene diamine and mixtures of terephthalic acid and isophthalic acid.

U.S. Patent 4,014,967 to Kirsch et al. provides thermoplastic polyamide molding compositions which
10 include at least one amorphous linear polyamide, and at least one segmented thermoplastic elastomeric copolyester; the elastomeric copolyester consist essentially of a large number of repeating intralinear long chain and short chain ester units linked head-to-
15 tail via ester linkages wherein both the long chain and short chain ester linkages are of a particular structure.

U.S. Patent 4,826,955 to Akkapeddi et al. provides an article of manufacture which comprises at least one
20 barrier layer of an amorphous nylon copolymer.

PCT International Application WO 91/13113 to Exxon Chemical Patents Inc. provides oxygen barrier structures comprising polyoxamides or copoly(amide-oxamide)s which may be derived from a reaction between
25 one or more diamines and oxalic acid, or derivative thereof. In Example 7 of that reference are discussed the copoly(amide-oxamide), nylon-MXD2/MXD6. The oxygen barrier layers find particular use in coextruded structures such a films.

30 Various other resins featuring reduced barrier characteristics may be found in "The Effect of Structure Upon the Oxygen Permeation Properties of Amorphous Polyamide" by TD Krizan, JC Coburn and PS Blatz, *Polymer Preprints*, 30, 9 (1989), which discusses
35 blends of nylon 66, and a poly(hexamethylene

isophthalamide/terephthalamide) resin. Further, in an article titled "Miscibility in blends of aliphatic polyamides and aromatic polyamide, nylon 3Me6T" by TS Ellis, published in *POLYMER*, 1988, Vol.29, (November), blends of nylon 6 and an amorphous aromatic polyamide, nylon 3Me6T, a condensation product of dimethyl terephthalate and 2,2,4,4-trimethyl-1,6-hexanediamine, and are discussed, and various nylons are discussed.

While these compositions provide useful thermoplastic compositions which find utility in the art, there nonetheless remains a real and continuing need for improved thermoplastic molding compositions which feature good physical characteristics, good vapour barrier properties and good process ability.

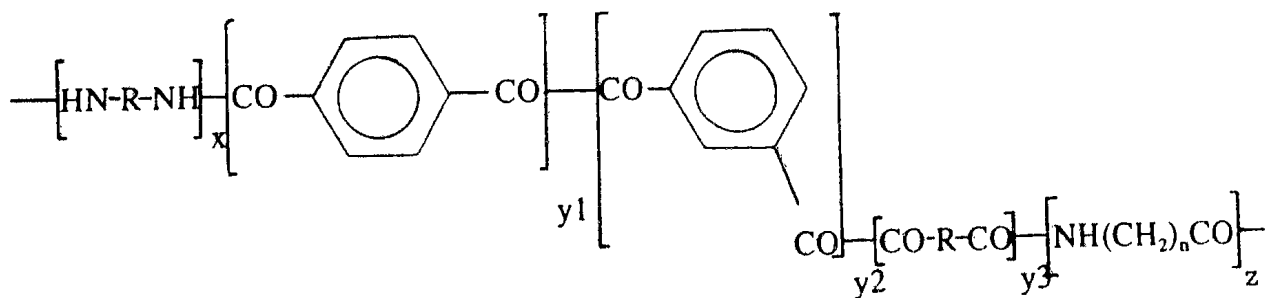
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SUMMARY

The present invention provides:

A thermoplastic polymeric composition comprising:

- (A) a first polyamide which is one or more aliphatic or cycloaliphatic polyamides; and
- (B) a second amorphous copolyamide which is represented by the following formula:



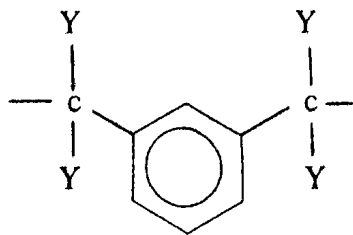
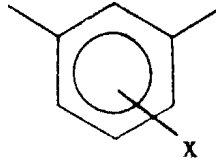
wherein:

$$x + y1 + y2 + y3 + z = 1$$

and,

$$y1 + y2 + y3 = x$$

wherein n has a value of 5 - 11, and $z = 0 - 0.5$ and wherein R may be selected from the group consisting of :



15 The present invention also provides a film formed from the thermoplastic polymeric composition as herein described.

The compositions of the present invention may further optionally comprise:

(C) conventional additives and processing aids which are known to the art which include but are not limited to: heat stabilizers, processing agents, lubricants, mold release agents, ultraviolet stabilizers, organic dyes and pigments, inorganic reinforcing materials, and plasticizing agents.

In a further aspect of the invention there is provided a thermoplastic polymeric molding composition as outlined above which features a glass transition temperature (sometimes hereinafter interchangeably referred to as " T_g ") which is higher than that of the conventional polyamide constituent (A) and is preferably equal to or in excess of 100°C as compared under like conditions, indicating a substantial degree of miscibility of the constituents of the blend composition.

In a yet further aspect of the invention there is provided a process for forming a thermoplastic polymeric molding composition which comprises at least the (A) conventional polyamide constituent and the (B) amorphous copolyamide constituent described above.

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In a still further aspect of the invention there is provided a plurality of articles including films, molded articles, profiled shapes, as well as articles comprising a layer of the composition in their construction.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides thermoplastic polymeric molding compositions comprising

10 (A) a first conventional polyamide, and
(B) an amorphous copolyamide which is polymerized from

(B₁) a polyamide forming monomer selected from the group consisting of lactams, aminoalkanoic acids and mixture thereof wherein the monomer is present in a molar proportion of between about 0 and 50%,

(B₂) a diamine selected from the group consisting of aralkylene diamines, cycloalkylene diamines and mixtures thereof, the diamine being present in a molar proportion of between about 25 and 60%,

20 (B₃) a dicarboxylic acid selected from the group of an aromatic dicarboxylic acid, aralkylene dicarboxylic acids, and aliphatic dicarboxylic acids; preferably the use of an aliphatic dicarboxylic acid in conjunction with an aromatic dicarboxylic acid is preferred, at least one aromatic diacid, the dicarboxylic acid being present in a molar proportion of between about 25 and 60%.

The compositions of the present invention may optionally further include

30 (C) conventional additives and processing aids which are known to the art which include but are not limited to: heat stabilizers, processing agents, lubricants, mold release agents, ultraviolet stabilizers, organic dyes and pigments, inorganic reinforcing materials, and plasticizing agents.

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Polyamides suitable for use with the instant invention and which are considered to be the conventional polyamides (A) in accordance with the present teaching include the long chain polymeric amides having recurring amide groups as part of the polymer backbone and preferably, have a number average molecular weight as measured by end group titration of about 15,000 to 40,000. The polyamides suitable for use herein can be produced by any conventional means known to the art.

Conventional polyamides (A) which find use in accordance with the present invention include those which may be obtained by the polymerization of equimolar proportions of a diamine having two or more carbon atoms between the amine terminal groups with a dicarboxylic acid, or alternately that obtained by the polymerization of a monoamino carboxylic acid or an internal lactam thereof with an equimolar proportion of a diamine and a dicarboxylic acid. Further, suitable polyamides may be derived by the condensation of a monoaminocarboxylic acid or an internal lactam thereof having at least two carbon atoms between the amino and the carboxylic acid groups, as well as other means. General procedures useful for the preparation of polyamides are well known to the art, and the details of their formation are well described under the heading "Polyamides" in the Encyclopedia of Polymer Science and Technology, published by John Wiley & Sons, Inc, Vol. 10, pps.487-491, (1969).

Suitable diamines include those having the formula

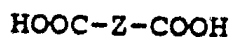


wherein n has an integer value of 1 - 16, and includes such compounds as trimethylenediamine,

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tetramethylenediamine, pentamethylenediamine,
hexamethylenediamine, octamethylenediamine,
decamethylenediamine, dodecamethylenediamine,
hexadecamethylenediamine, aromatic diamines such as p-
5 phenylenediamine, 4,4'-diaminodiphenyl ether, 4,4'-
diaminodiphenyl sulphone, 4,4'-diaminodiphenylmethane,
alkylated diamines such as 2,2-
dimethylpentamethylenediamine, 2,2,4-
trimethylhexamethylenediamine, and 2,4,4-
10 trimethylpentamethylenediamine, as well as
cycloaliphatic diamines, such as
diaminodicyclohexylmethane, and other compounds.

The dicarboxylic acids useful in the formation of
polyamides are preferably those which are represented
15 by the general formula



wherein Z is representative of a divalent aliphatic
20 radical containing at least 2 carbon atoms, such as
adipic acid, sebacic acid, octadecanedioic acid,
pimelic acid, subeic acid, azelaic acid, undecanedioic
acid, and glutaric acid. The dicarboxylic acids may be
aliphatic acids, or aromatic acids, such as isophthalic
25 acid and terephthalic acid.

By means of example, suitable polyamides include:
polypyrrolidone (nylon 4), polycaprolactam (nylon 6),
polyheptanolactam (nylon 7), polycaprylactam (nylon 8),
polynonanolactam (nylon 9), polyundecaneolactam (nylon
30 11), polydodecanolactam (nylon 12),
poly(tetramethylenediamine-co-oxalic acid) (nylon 4,2),
poly(tetramethylenediamine-co-adipic acid) (nylon 4,6),
poly(tetramethylenediamine-co-isophthalic acid) (nylon
4,I), polyhexamethylene azelaamide (nylon 6,9),
35 polyhexamethylene sebacamide (nylon 6,10),

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polyhexamethylene isophthalamide (nylon 6,IP),
polymetaxylylene adipamide (nylon MXD6), the polyamide
of n-dodecanedioic acid and hexamethylenediamine (nylon
6,12), the polyamide of dodecamethylenediamine and n-
5 dodecanedioic acid (nylon 12,12), as well as copolymers
thereof which include: hexamethylene adipamide-
caprolactam (nylon 6,6/6), hexamethylene
adipamide/hexamethylene-isophthalamide (nylon 6,6/6IP),
hexamethylene adipamide/hexamethylene-terephthalamide
10 (nylon 6,6/6T), trimethylene adipamide-hexamethylene-
azelaicamide (nylon trimethyl 6,2/6,2), and
hexamethylene adipamide-hexamethylene-azelaicamide
caprolactam (nylon 6,6/6,9/6) as well as others which
are not particularly delineated here.

15 Of these, the preferred conventional polyamides
include polyhexamethylene adipamide (nylon 12) and
polycaprolactam (nylon 6).

The (B) amorphous copolyamide which which forms a
second essential constituent of the present invention
20 is at least one which is is polymerized from

(B₁) a polyamide forming monomer selected from the
group consisting of lactams, aminoalkanoic acids and
mixture thereof wherein the monomer is present in a
molar proportion of between about 0 and 50%,

25 (B₂) a diamine selected from the group consisting
of aralkylene diamines, cycloalkylene diamines and
mixtures thereof, the diamine being present in a molar
proportion of between about 25 and 60%,

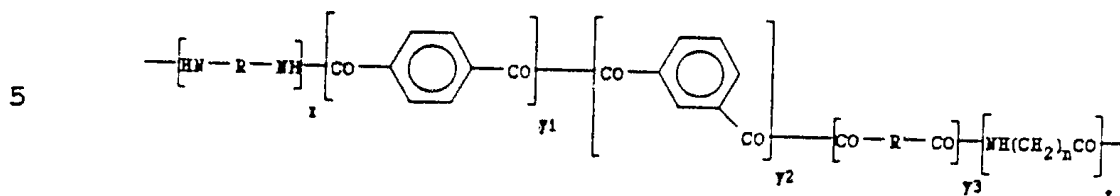
(B₃) an acid selected from the group of aromatic
30 dicarboxylic acids, aralkylene dicarboxylic acids, and
aliphatic dicarboxylic acids. It is preferred that an
aromatic dicarboxylic acid in conjunction with an
aliphatic dicarboxylic acid be used. The acid B₃ being
present in a molar proportion of between about 25 and
35 60%.

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These materials and methods for their production are particularly described in U.S. Patent 4,826,955 the contents of which are wholly incorporated by reference.

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The amorphous copolyamide (B) may generally be represented by the following formula:



10 wherein;

the subscripts to the parenthesis in the equation are representative of mole fractions of each of the indicated segments of the amorphous copolyamide (B) such that:

15
$$x + y_1 + y_2 + y_3 + z = 1 \quad [\text{Eq.1}]$$

and,

$$y_1 + y_2 + y_3 = x \quad [\text{Eq.2}]$$

and wherein "n" has a value of 5 - 11, and $z = 0 - 0.5$.

20 The constituent "R" in the structure above may be any one or more of the following:



"X" may be $-\text{CH}_3$, an n-alkyl group, or a halide such as $-\text{Cl}$,

"Y" may be H or $-\text{CH}_3$,

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"R" is an α,ω -alkylene radical containing 4 to 18 carbon atoms particularly including those derived from adipic acid, azelaic acid, sebacic acid and dodecanedioic acid.

5 The polyamide forming monomer (B_1) is at least one monomer selected from the group consisting of: lactams, aminoalkanoic acids. Exemplary materials include the C_5 - C_{12} lactams as well as their corresponding aminoalkanoic acids such as caprolactam, lauoyllactam,
10 ϵ -aminocaproic acid, ω -aminolauric acid, 11-aminoundecanoic acid, 12-aminododecanoic acid, aminomethylbenzoic acid, and the like. Mixtures of two or more of the above are also contemplated. Of these, the preferred monomer is caprolactam.

15 The diamine (B_2) is one or more diamines selected from the group consisting of aralkylene diamines, and cycloalkylene diamines.

 Exemplary diamines (B_2) include aralkyldiamines, as well as mixtures thereof. Such diamines include but
20 are not limited to:

m-bis-(aminoalkylbenzenes),
p-bis-(aminoalkylbenzenes), such as m-xylylene diamine and p-xylylene diamine, as well as mixtures thereof,
m-bis-(aminoethylbenzene),
25 p-bis-(aminoethylbenzene),
2,4-bis-(aminomethyl) chlorobenzene and the like.
Exemplary diamines (B_2) further include aromatic diamines such as toluene-2,4-diamine (which may optionally include minor amounts of toluene-2,6-
30 diamine), 4,4'-methylenediamine, 4,4'-oxydiamine, 4,4'-sulfonyldiamine, 3,3'-dimethyl-4,4'-methylene diamine.

 Additionally, it is contemplated that in the place of aromatic diamines discussed here that the corresponding diisocyanates may also be used as a
35 monomer constituent for (B_2).

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It is further contemplated that in the place of the aromatic diamines discussed here that polyoxamides or copoly(amide-oxamides) may be utilized as the monomer constituent for (B₂). Such polyoxamides are the reaction product of oxalic acid, or derivative thereof with at least one diamine by conventional techniques, including melt, interfacial or solution polymerization techniques. Polyoxamides which may be used include: poly(ethylene oxamide), poly(trimethylene oxamide), poly(tetra-methylene oxamide), poly(pentamethylene oxamide), poly(hexamethylene oxamide), poly(heptamethylene oxamide), poly(octamethylene oxamide), poly(nonamethylene oxamide), poly(decamethylene oxamide), poly(dodecamethylene oxamide), poly(hexamethylene/octamethylene oxamide), poly(hexamethylene/decamethylene oxamide), poly(hexamethylene/trimethylhexamethylene oxamide), as well as poly(m-xylylene oxamide).

Copoly(amide-oxamides) which find use include those which are the reaction product of at least one diamine with oxalic acid or derivative thereof and further, at least one or more dicarboxylic acids; or the reaction of one or more monoaminomonocarboxylic acids or derivatives or lactams thereof, with one or more diamines and oxalic acid, and optionally, one or more dicarboxylic acids. The copoly(amide-oxamides) may be formed by conventional techniques including melt, interfacial or solution polymerization techniques. The copoly(amide-oxamide) may be random, block, or regularly alternating type copolymers.

Specific copoly(amide-oxamides) which may be used in the practice of the present invention include poly(hexamethylene oxamide/azelamide), poly(hexamethylene oxamide/sebacamide),

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poly(hexamethylene oxamide/isophthalamide),
poly(hexamethylene oxamide, terephthalamide), poly(m-
xylylene oxamide/m-xylylene adipamide), as well as
others, including those described in PCT/US91/01083.

5 Particularly preferred diamines (B_2) include:
m-xylylene diamine (sometimes interchangeably referred
to as "MXDA"), poly(m-xylylene oxamide/m-xylylene
adipamide) (sometimes interchangeably referred to as
"nylon-MXD2/MXD6"), p-xylylene diamine (sometimes
10 interchangeably referred to as "PXDA"),
bis-(p-aminocyclohexyl) methane (sometimes
interchangeably referred to herein as "PACM"),
1,3-bis-(aminomethyl) cyclohexane, and,
1-methyl 2,4-diaminocyclohexane. The most preferred
15 diamine (B_2) is MXDA which may comprise some of the
para isomer.

It is to be understood that mixtures of two or
more of the above diamines or other suitable
constituents described above may be used as the diamine
20 constituent (B_2).

A further essential constituent (B_3) is at least
one aromatic diacid including aromatic dicarboxylic
acids having 7 to 20 carbon atoms, including
terephthalic acid (interchangeably referred to as
25 "TPA"),
isophthalic acid (interchangeably referred to as
"IPA"),
t-butylisophthalic acid,
3-(4-carboxyphenyl-1,1,3-trimethyl-5-indan carboxylic
30 acid (interchangeably referred to as "PIDA"), and which
is also known as phenylindane dicarboxylic acid, or
more broadly simply as a phenylene diacid,
2,6-naphthalene-dicarboxylic acid, and the like.

Further, the ester derivative of the diacid may be
35 used in place of or in conjunction with its

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corresponding diacid, i.e., diphenyl or dimethyl terephthalate may be used in the stead of TPA; hence, the diacid (B₃) is also to be understood to include such ester derivatives.

5 Mixtures of two or more of the above diacids and/or ester derivatives are contemplated as useful in forming the diacid (B₃).

 Preferably, the diacid (B₃) include mixtures of IPA, TPA, and PIDA, and most preferably include
10 mixtures of terephthalic acid and isophthalic acid.

 The (B₁), (B₂) and (B₃) constituents may be present in an approximate molar proportion of (B₁):(B₂):(B₃) of 0-50%:25-60%:25-60%. Preferably the approximate molar ratios are within the proportions of
15 20-50%:30-50%:30-50%. Most preferably the approximate molar ratios of these constituents are within the respective molar proportions of 30-40%:30-40%:30-40%. It is further preferred that approximately equal molar amounts of (B₂) and (B₃) be used.

20 The present inventors have found that if component (B₁) is present in an amount greater than that described above, the resulting amorphous copolymer (B) features poor oxygen barrier resistance in humid environments. Poor oxygen barrier resistance in humid
25 environments also results when B₂ and B₃ are present in amounts less than those outlined above.

 The amorphous copolymer (B) may be any type of copolymer, such as a random copolymer, block copolymer, graft or "branched" copolymers, repeating copolymers
30 and others not particularly described here.

 The amorphous copolymer (B) may be produced by methods which are known to the art for the production of polyamides. For example, in the case of copolymers formed from caprolatam, MXDA, IPA and TPA, all of the
35 constituents may be charged to a reactor vessel

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followed by heating to an appropriate reaction temperature, generally approx. 200-325°C, under a blanketed of an inert gas such as nitrogen or argon. In an alternative method, in the case of copolymers formed from caprolactam, MXDA, IPA and TPA, the salt of MXDA and the salt of the IPA/TPA may be formed in situ and added as a preformed salt, followed by the addition of caprolactam. Water may be used as a solvent in the initial stages of the formation of the salts.

Further methods for the production of the amorphous copolyamide (B) are more particularly detailed in commonly assigned U.S. Patent 4,826,955, the contents of which are herein incorporated by reference.

The amorphous copolyamide (B) according to the present invention is a transparent, amorphous polymer having a dry Tg of at least 100°C but preferably in the range of 130°C - 290°C, and preferably further includes a "wet" Tg ("wet" being understood as 100% relative humidity) of at least 25°C, more preferably in excess of 40°C.

The amorphous copolyamide (B) according to the invention has a reduced solution viscosity in m-cresol at 25°C of at least about 0.5 dl/g, preferably between about 0.7 and 1.2 dl/g.

The thermoplastic polymeric molding compositions may comprise the conventional polyamide (A) and the amorphous copolyamide (B) in any amount wherein there is realized by the composition an improvement in the modulus, yield stress and/or oxygen barrier properties, particularly when exposed under humid conditions, over the modulus, yield stress and/or oxygen barrier property of the conventional polyamide (A) under like conditions. Preferably, a thermoplastic polymeric molding composition comprises in terms of percentage by

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weight at least 5% (B). More preferably, an inventive composition comprises between 50-95% (A) and 5-50% (B).

An advantageous feature of the instant invention is that there are provided specific compositions which
5 comprise conventional polyamides, particularly those known to the art as nylon 6 and nylon 66 (as well as mixtures and copolymers comprising the same) wherein certain shortcomings in the prior art are overcome. More particularly, the glass transition temperatures
10 and the barrier properties of the conventional nylons are improved by the addition of the amorphous copolyamides (B) taught herein and that such resultant thermoplastic molding composition is useful as a molding composition useful in the formation of articles
15 therefrom. Further, such articles simultaneously feature excellent physical characteristics which are very similar to that of the conventional polyamide (A) constituent alone, under like conditions. This is particularly appreciable under conditions of relatively
20 high humidity, i.e., 25% and greater relative humidity, particularly at conditions of 100% relative humidity; the inventive compositions exhibit reduced sensitivity to moisture and provide excellent barrier properties and good physical characteristics.

25 The inventor have surprisingly also found that the inventive compositions provide improvements in the yield stress and improvements in the barrier characteristics, especially under humid conditions, when even minor amounts of the amorphous copolyamide
30 (B) are included in the composition. Whereas one skilled in the art would expect that one might at best realize improvements in the various characteristics of a composition which would be directly proportional to the amount of the amorphous copolyamide (B) relative to
35 the amount of the conventional polyamide (A) included

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in a composition, it has been found that such a relationship is not realized. Rather, it has been found that significant improvements in the barrier properties, particularly at relatively high humidity and at 100% humidity are realized when amounts as little as 35% and even less of the amorphous copolyamide (B) are included. The compositions also feature an increase in the melt temperature. This effect will be more particularly appreciated from the accompanying Examples presented below.

The thermoplastic molding compositions according to the present invention is produced by conventional means known to the art of the production and processing of polyamide compositions. Blending or mixing of the constituents which comprise the composition may be by any effective means which will effect their uniform dispersion. All of the constituents may be mixed simultaneously or separately by a mixer, blender, kneader, roll, extruder, or the like in order to assure a uniform blend of the constituents. In the alternative, two or more but less than all of the constituents may be blended or mixed by mixer, blender, kneader, roll, extruder, or the like in order to assure a uniform blend of the constituents and the resultant mixture is melt-kneaded with the remaining constituents in an extruder to make a uniform blend. The most common method is to melt-knead a previously dry-blended composition further in a heated extruder provided with a single-screw, or in the alternative, a plurality of screws, extrude the uniform composition into strands extrude the uniform composition into strands, and subsequently chopping the extruded strands into pellets. The resulting molding composition may be subsequently provided to the feed hopper of a molding

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apparatus used for forming articles, or alternately, the molding composition may be stored.

The compositions according to the present invention may further include conventional additives
5 and processing aids which are known to the art. Typically such conventional additives are added to the composition in a mixing step and are included in an extrudate of the composition.

Heat stabilizers and processing agents include
10 those which are known to be useful in conjunction with thermoplastic compositions, and include halides of metals of Group I of the periodic table of elements, including but not limited to sodium halides, lithium halides, potassium halides as well as such halides in
15 conjunctive use with copper halides. Further stabilizers include sterically hindered phenols, hydroquinones as well as derivatives thereof. Generally such stabilizers and processing agents comprise 5 weight percent or less of a total
20 thermoplastic composition. Preferably such stabilizers and processing agents comprise 2.5 weight percent or less of a total thermoplastic composition.

Conventional lubricants and mold release agents which may be used include stearyl alcohol and fatty
25 acid esters, including stearic esters. Generally such lubricants and mold release agents comprise 5 weight percent or less of a total thermoplastic composition, preferably they comprise 2.5 weight percent or less of a total thermoplastic composition.

30 Ultraviolet stabilizers which may be used include any conventionally used UV stabilizers, non-limiting examples of which include substituted resorcinols, salicylates, benzotriazoles, benzophenones, as well as other materials. Generally such UV stabilizing agents
35 comprise 5 weight percent or less of a total

- 20 -

thermoplastic composition, preferably they comprise 2.5 weight percent or less of a total thermoplastic composition.

Conventionally used organic dyes and pigments may also be included in the compositions. Examples of such organic dyes and pigments include carbon black, ultramarine blue, dyes based on phthalocyanide, titanium dioxide, cadmium sulfide, cadmium sulfide selenide, nigrosine, as well as others. These conventionally used dyes and pigments may be included to comprise 10 weight percent or less of the total thermoplastic composition, preferably 5 weight percent or less.

Inorganic reinforcing materials as well as fibrous and powdered fillers may be advantageously included in the present inventive compositions. Examples of such conventionally known materials include glass beads or spheres, powdered glass, carbon fibers, glass fibers, asbestos, calcium silicate, calcium metasilicate, aluminum silicate, amorphous silica, fumed silica, magnesium carbonate, kaolin, powdered quartz, chalk, feldspar, and mica. Such reinforcing materials may comprise up to 65 weight percent of the total of the molding compositions, but is preferably 50 weight percent or less of the molding composition.

Further useful additives include nucleation promoters which are known to be useful in conjunction with polyamide compositions. Non-limiting examples of such materials include talc, calcium fluoride, alumina, sodium phenylphosphinate, polytetrafluoroethylene particularly in a finely divided form, as well as others. These conventionally used nucleation promoters may be included to comprise 10 weight percent or less of the total thermoplastic composition within which

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they are used, and are preferably 5 weight percent or less of the total thermoplastic composition.

Conventionally known plasticizing agents may form a part of the compositions taught herein. By way of example, but not of limitation, such plasticizing agents include dioctyl phthalate, dibenzyl phthalate, butylbenzyl phthalate, hydrocarbon oils, p-tolueneethylsulfonamide, and n-(n-butyl)-bensenesulfonamide, as well as others. The plasticizing agents may be included so to comprise about 35 weight percent or less of the total composition; preferably the plasticizing agents are present in amounts of less than 20 weight percent.

The composition of the present invention may be used for the production of articles formable from thermoplastic materials. By way of example and not of limitation, such articles include sheets, films, rods, tubes, profiled shapes, coatings, parisons for blow molding, as well as others not particularly denoted here. The compositions of the present invention also find particular utility in forming a barrier layer in a rigid molded article such as a flask, or in a flexible molded article such as a container comprising a flexible or semi-rigid structure. Such flexible and/or semi-rigid structures include films, and so called "thin-walled" structures which are plastically deformable but at least partially elastic.

Typically, the composition will be used to form products by injection molding a quantity of the composition which has been previously produced by an extrusion process into pellets, by first heating the preformed pellets to a fluid melt under the action of applied heat, compression and shear effects, and subsequently forcing a quantity of the said melted composition into mold or form where it is allowed to

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solidify, or in the case where such a composition is used to form a film therefrom, forcing a quantity of the said melted composition through a film die, such as a flat film die or a circular blown film die, and forming a film therefrom. In the case where the composition is used to form a film therefrom, it is contemplated that the films may be unoriented, or may be subjected to a conventional operation to impart a degree of orientation on the film. Such a film may be oriented in one direction, such as in the machine direction, such as in the "machine direction" and/or the "transverse direction", or may be oriented in both directions, or "biaxially" oriented.

The compositions taught in the present specification provide thermoplastic blend compositions which feature good physical properties, i.e., strength, toughness, heat resistance, chemical resistance, etc. which is known to the art as characteristic of non-amorphous polyamides. Particular reference is made here to polyhexamethylene adipamide (nylon 12) and polycaprolactam (nylon 6), as well as copolymers containing one or more of the above. The compositions taught in the present specification additionally feature excellent retention of the modulus of the compositions which are relatively insensitive to increasing levels of moisture. Such properties are especially suited for applications where retention of physical properties, and good gas barrier properties, such as oxygen barrier, aroma barrier, etc. are desired. Uses wherein such characteristics are desirable include in the manufacture of films formed from or comprising the compositions taught herein, as well as articles for the containment of liquids and solids sensitive to moisture or contact with gases or aromas.

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The foregoing invention will be more apparent by reference to specific embodiments which are representative of the invention. It is nonetheless to be understood that the particular embodiments described herein are provided for the purpose of illustration, and not be means of limitation, and that it is to be further understood that the present invention may be practiced in a manner which is not exemplified herein without departing from its scope.

EXAMPLES

In the following embodiments of the invention, it is to be understood that in the description of any composition, all percentages associated with a constituent used to form a composition are to be understood as to be "percentage by weight" of the particular constituent relative to the composition of which it forms a part. Exceptions to this convention will be particularly noted.

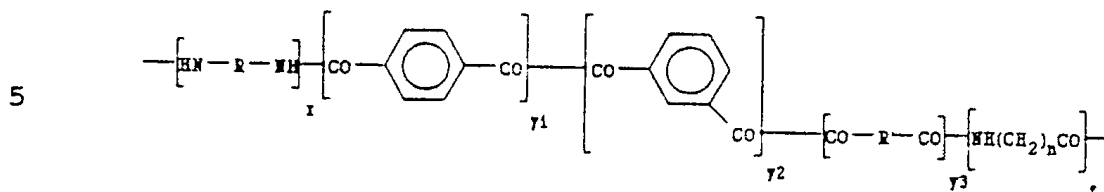
EXAMPLE 1 - Production of amorphous copolyamide (I)

An amorphous copolymer was produced in accordance with following: there is charged to a reaction kettle 32.2 gm of caprolactam, 1.7 gm aminocaproic acid (which is provided as an additional initiator), 19.9 gm of terephthalic acid ("TPA"), 19.9 gm of isophthalic acid, ("IPA"), and 18.5 gm of phenylindane dicarboxylic acid ("PIDA").

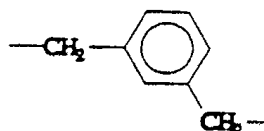
The kettle was sealed and an argon sweep was directed at its contents for 30 minutes, afterwards 40.8 gm of meta-xylylenediamine ("MXDA") was added, and the argon sweep continued for a further period of 15 minutes.

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The copolyamide produced had the structure:



wherein the value were as follows: $x = 0.34$, $y_1 = y_2 = 0.17$, $y_3 = 0$, $z = 0.32$, $n = 5$, and wherein the
10 substituent "R" had the structure:



The contents of the kettle was then heated starting at 125°C, and then raised in 25°C steps to a final temperature of 275°C. The time interval of each period varied between 30 minutes to 2 hours, except for
20 the final period where the heating was continued at 275°C until the reaction mixture became too viscous to stir or in the alternative, no further change in viscosity was noted.

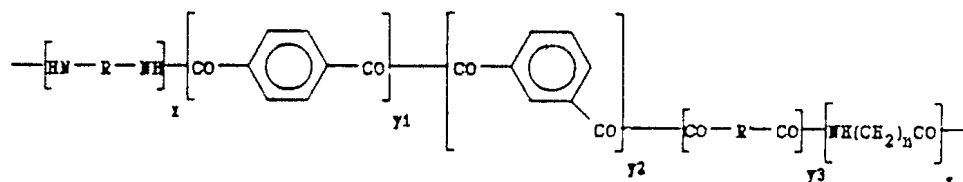
The product produced was transparent, and showed
25 no crystalline endotherm in a DSC analysis.

EXAMPLE 2 - Production of amorphous copolyamide (II)

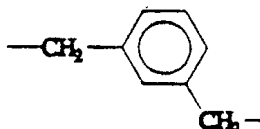
To produce an MXDA/IPA/TPA based amorphous polyamide by an interfacial polymerization technique,
30 3.05 grams of isophthaloyl chloride and 3.05 grams of terephthaloyl chloride were dissolved in 300 ml of ethylene chloride. The resultant solution was placed in a clean, dry addition funnel. In a second flask 4.086 grams of m-xylene diamine and 6.36 grams of
35 sodium carbonate were dissolved in 500 ml of water.

- 25 -

The contents of this second flask was a solution which was then transferred to a laboratory blender. The aqueous solution was then agitated, during which the ethylene chloride solution was added in a drop-wise manner. A fluffy white polymer precipitate resulted. This polymer precipitate was filtered, washed, and then dried under vacuum to remove any residual solvents. Total yield was approximately 96% of theoretical yield. The copolyamide produced had the structure:



wherein the values of the substituents were as follows: $x = 0.5$, $y1 = y2 = 0.25$, $y3 = z = 0$, and wherein the substituent "R" had the structure:



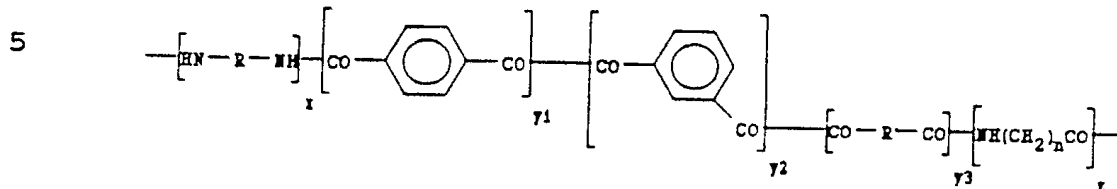
This sample and other like samples prepared in this manner were later determined to have intrinsic viscosities ranging from 0.60 to 0.80. Differential scanning calorimetry of the samples showed that the polymer had a glass transition temperature of about 184°C. No melting peak was observed, indicating that the polymer was amorphous.

EXAMPLE 3 - Production of amorphous copolyamide (III)

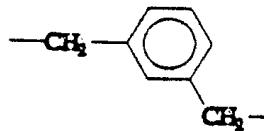
An amorphous polyamide was produced in accordance with a melt polymerization technique using the conditions generally in accordance with Example 1 above. The constituents included meta-xylylenediamine

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and isophthalic acid. The copolyamide produced had the structure:



wherein the values of the substituents were as follows:
 10 $x = y_2 = 0.5$; $y_1 = y_3 = z = 0$, and wherein the
 substituent "R" had the structure:

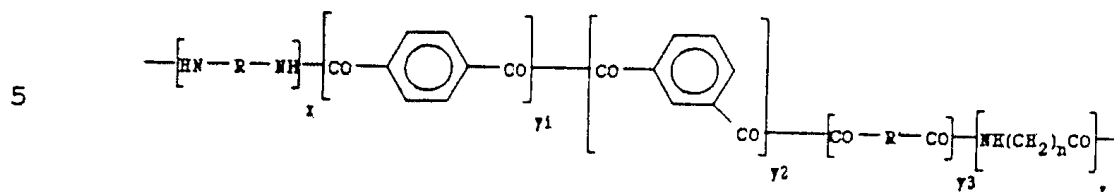


EXAMPLE 4 - Production of amorphous copolyamide (IV)

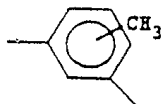
An amorphous polyamide was produced in accordance
 20 with a solution polymerization technique using the
 conditions generally in accordance with Example 2
 above. The constituents included toluene-2,4-diamine
 and isophthaloyl chloride. Methylene chloride was used
 as the solvent, and triethyl amine was used as the
 25 base.

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The copolyamide produced had the structure:



wherein the values of the substituents were as follows:
 10 $x = y_2 = 0.5$; $y_1 = y_3 = z = 0$, and wherein the
 substituent "R" had the structure:



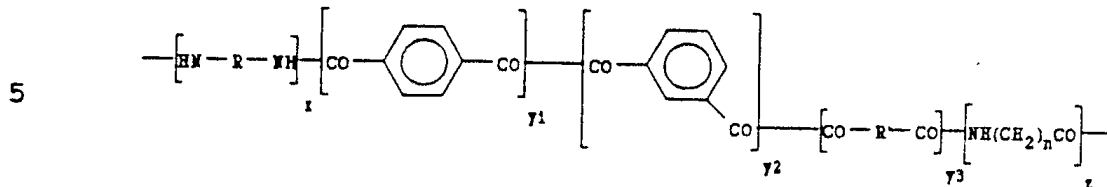
15

EXAMPLE 5 - Production of amorphous copolyamide (V)

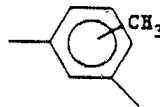
An amorphous polyamide similar to that produced as
 Example 4 was produced using the solution
 polymerization conditions generally in accordance with
 20 Example 4 above. The constituents included toluene-
 2,4-diamine or toluene-2,6-diamine and isophthaloyl
 chloride. As a further comonomer adipoyl chloride was
 also provided to the reaction mixture. Methylene
 chloride was used as the solvent, and triethyl amine
 25 was used as the base.

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The copolyamide produced had the structure:



wherein the values of the substituents were as follows:
 10 $x = 0.5$; $y_2 = 0.4$; $y_1 = 0$; $y_3 = 0.1$; $z = 0$, and wherein
 the substituent "R" had the structure:



15

Preparation of Blend Compositions

20 Compositions according to the present invention's
 teaching were prepared. As the constituent (A), the
 conventional polyamide used was Capron® 8202, a
 commercially available nylon-6 molding grade
 homopolymer resin which includes the following physical
 characteristics: a specific gravity of about 1.13
 25 according to ASTM D-792, a melting point of about 420°F
 (215°C) according to ASTM D-789, a yield tensile
 strength of approximately 11,500 psi (80 MPa) according
 to ASTM D-638, an ultimate elongation of about 70%
 according to ASTM D-638, a flexural strength according
 30 to ASTM D-790 of about 15,700 psi (110 MPa), a flexural
 modulus according to ASTM D-790 of about 410,000 psi
 (2,825 MPa). As the amorphous polyamide (B),
 compositions according to Examples 1 through 4 were
 used.

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Blended molding compositions were prepared generally in accordance with one the following procedures.

5 Melt Blending (1) - Single Screw Extruder

To a Killion 1" single screw extruder having a length:diameter ratio of 30:1 and provided with a general purpose mixing screw were provided a tumble blended mixture of proportional amounts of (A) which
10 had been ground to a powder using a Wiley mill, and proportional amounts of an amorphous copolyamide (B) in accordance with Examples 1 through 4. The extruder was operated at 280°C to plastificate and melt mix the constituents and the extrudate was forced through a
15 coathanger type flat film forming die to form a film having a thickness of approximately 1-2 mils [0.004 - 0.008 cm] and a width of approximately 6 inches [15.25 cm].

20 Melt Blending (2) - Twin-screw Extruder

To a HBI twin screw extruder was provided a tumble blended mixture of proportional amounts of (A) and proportional amounts of an amorphous copolyamide (B) in accordance with Examples 1 through 5 and designated as
25 "Amorphous Copolyamide Type I-V" respectively. The extruder was operated at 280°C to plastificate and melt mix the constituents and the extrudate was forced through a strand forming die which formed the extrudate into strands of approximately 1/8" diameter which were
30 rapidly quenched in a water bath, and subsequently pelletized.

Solution Blending

To a 500 ml 3-neck round bottom flask fitted with
35 a condenser, mechanical stirrer, nitrogen purge, and

- 30 -

heating mantle was charged a proportional amount of (A) and a respective proportional amount of an amorphous copolymer (B) as well as 200 ml of trifluoroethanol. By a "proportional amount" it is to be understood that
5 in the formation of a blend, proportional weights of (A) and (B) were provided, i.e., in a 50%/50% blend equal amounts of (A) and (B) were provided; in a 75%/25% blend, three times as much (A) was provided as (B).

10 The mixture was stirred for 60 minutes, then heated to reflux and stirred overnight. Afterwards, the mixture was allowed to cool, and then added dropwise into a beaker containing 600 ml of diethylether. A fluffy white precipitate formed, which was
15 subsequently filtered, washed, and dried under vacuum to remove any traces of solvent. Resultant blends were then evaluated using differential scanning calorimetry techniques (DSC).

20

Physical Properties

Evaluation of the physical properties of the blended molding compositions included standard physical testing according to ASTM D-638 test protocols using standard 1/8" thick ASTM tensile bars. To evaluate the
25 effect of moisture on the tensile yield strength of blended molding compositions, the bars were first tested in their as molded state, and subsequently like samples were conditioned in a 50% relative humidity chamber at approximately 20-25°C for a period of 8
30 weeks, after which the samples were again retested in accordance with ASTM D-638 protocols.

Evaluation of the DSC melting points and glass transition temperature for the various samples was performed using a DuPont 9900 DSC apparatus or a
35 Mettler DSC-30 apparatus. The "wet" Tg measurements

- 31 -

were performed on film samples which were pre-equilibrated with water and finely chopped before being placed in a stainless steel DSC sample pan. The pans were then sealed by placing a further stainless steel DSC pan and tightly crimping the DSC pans to so provide a tight seal. Subsequently, the DSC evaluation was performed in a conventional manner using a heating rate of 10°C/minute; the crimped sealed pans ensured that water did not escape from the samples being tested. The moisture content of a respective sample was also independently monitored by thermogravimetric analysis on selective samples; in all other cases a gravimetric method was used to ensure saturated water absorption.

Evaluation of the vapor barrier properties of a respective composition was performed on film samples having a thickness of approximately 1-2 mils [0.004-0.008 cm] produced with the procedure outlined as Melt Blending (1) above. Testing of the film sample was performed using a Permatran MOCON OxTrans analyzer operating in an automatic mode. Results provided report oxygen transmission of the respective sample at a condition of 100% (or 90% as may be particularly denoted) relative humidity ("wet") of cubic centimeters of oxygen transmitted per mil of film for a 100 square inch area of film per day.

Table 1 lists certain physical characteristics of the various amorphous copolyamides (B) indicated as Type I - V copolyamides in accordance with the present inventive teaching, as well as a conventional polyamide (A), viz., nylon 6.

TABLE 1 - Amorphous Nylons

Amorphous Copolyamide type:	Tg (deg.C)		Oxygen Permeability:	
	"dry"	"wet"	"dry"	"wet"
I	125	50 (54)	1.3	0.2
II	190	-	-	-
III	170	68	0.5	0.1
IV	270	137	-	-
V	238	128	-	-

- "wet" Tg values at 100 % relative humidity

- Oxygen Permeability reported as (cc oxygen per mil thickness/100 sq.inches/day

- Tg values indicate DSC onset and (mid-point) values

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Test results are indicated on Tables 2 and 3 following; Table 2 lists particular physical properties of blend molding compositions which comprised the polyamide (A) and the Type I amorphous polyamide (B) according to Example 1.

Table 2 lists a series of compositions of which "C1" is a comparative example consisting essentially of the polyamide (A), and numbered Examples 1-7 indicate blend compositions according to the present invention which were formed into films having a thickness of 1-2 mils as described above. As should be readily apparent from the results, the addition of even minor amounts of the (B) to blend compositions comprising (A) and (B) are shown to provide significant improvements in the "wet" glass transition temperatures and oxygen permeability of the blends as compared to the conventional polyamide (A). All of the compositions of Examples 1-7 were first formed by melt blending (A) and (B) in a twin screw extruder, pelletizing the extrudate, which pellets were subsequently used to form films.

TABLE 2 - Nylon 6 / Amorphous Nylon Blends

Example	Amorphous Copolyamide type:	Blend Ratio (A):(B)	Tg (deg.C)		Oxygen Permeability:	
			"dry"	"wet"	"dry"	"wet"
C1	---	100:0	45(50)	-15	2.85	14.8
1	I	80:20	57	—	2.56	2.1 *
2	I	75:25	—	3	—	—
3	I	70:30	81	—	2.3	6.17
4	I	50:50	79(85)	19(30)	1.97	2.6
5	I	40:60	94	—	1.9	0.36 *
6	I	30:70	—	—	1.58	3.27
7	I	15:85	110	34(40)	—	—

- "wet" Tg values at 100 % relative humidity
- Oxygen Permeability reported as (cc oxygen per mil thickness/100 sq.Inches/day)
- Oxygen Permeability "wet" values with * are at 90% relative humidity; all others at 100% relative humidity
- Tg values indicate DSC onset and (mid-point) values

TABLE 3 - Nylon 6/66 (85/15) copolymer / Amorphous Nylon Blends

Example:	Amorphous Copolyamide type:	Blend Ratio (A):(B)	Oxygen Permeability:	
			"dry"	"wet"
C3	-	100:0	3.3	21.6
8	I	75:25	2.5	8.8
9	I	60:40	2.8	6.2
10	I	50:50	2.2	4.6
11	I	25:75	1.7	4.2

- "wet" Tg values at 100 % relative humidity

- Oxygen Permeability reported as (cc oxygen per mil thickness/100 sq.inches/day)

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Table 3 lists glass transition temperatures of blend molding compositions comprising a further polyamide (A) and the Type I amorphous copolyamide (B). The further polyamide (A) of Table 2 is a nylon 6/66 polyamide having a weight ratio of nylon 6:nylon 66 segments of 85 wt%:15 wt%. This nylon 6/66 polyamide is presently commercially available from Allied Signal Corp., Morristown, NJ USA under the trade designation of "XPN-1539" or alternately in a film as "Capron® Extraform®".

The compositions of Table 3 provide a comparative example "C3" which consists essentially of the nylon 6/66 polyamide, and further blend compositions according to the invention which are presented as numbered Examples 8-11. All of the example compositions according to Table 2 were formed into films having a thickness of 1-2 mils in accordance with the protocol outlined above for the compositions of Examples 1-7. Of particular note regarding the reported data is that each of the blend samples tested provided a single glass transition temperature in both "dry" and in "wet" (100% relative humidity) test conditions indicating the miscibility of both polyamides (A) and (B) within the blend composition.

As may be seen from Table 3, the addition of even minor proportions of (B) to the blend compositions comprising (A) and (B) provides significant improvement in the oxygen barrier characteristics of the samples.

Shown on Table 4 are physical test results of further Example blend compositions numbered 12 and 13 according to the present invention, and a Comparative Example "C1" which consists essentially of Capron® 8202. The compositions were formed into standard 1/8 inch testing bars and subjected to evaluation under "dry" and "wet" conditions. As may be seen from the

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reported results on Table 4, the blend compositions show improved retention of yield strength when subjected to the adverse environmental condition of 100% humidity.

TABLE 4 - Nylon 6 / Amorphous Nylon Blends

Example	Amorphous Copolyamide type:	Blend Ratio (A):(B)	Yield Strength, kpsi [kPa]		Yld.Str. Retention
			"dry"	"wet"	
C1	--	100:0	11.1 [5202]	7.7 [3609]	69 %
12	I	75:25	12.4 [5812]	9.6 [4500]	77 %
13	I	50:50	13.9 [6515]	13.6 [6375]	98 %

- "wet" Tg values at 100 % relative humidity

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Table 5 illustrates further Example compositions 14-24 of various blends of a conventional polyamide (A) which is Capron® 8202, and different amorphous copolyamides (B) of Types II, III, IV, and V described above forming blend compositions according to the present invention. The compositions of Examples 14-17, and Examples 21-24 were formed by a the Solution Blending technique previously described which were then extruded into films; the compositions of Examples 18-20 were formed by melt blending (A) and (B) in a twin screw extruder, pelletizing the extrudate, which pellets were subsequently used to form films. The films of Examples 14-24 had thicknesses of 1-2 mils.

TABLE 5 - Nylon 6 / Amorphous Nylon Blends

Example	Amorphous Copolyamide type:	Blend Ratio (A):(B)	Tg (deg.C)		Oxygen Permeability:	
			"dry"	"wet"	"dry"	"wet"
C1	—	100:0	45(50)	-15	2.85	14.8
14	II	90:10	70	-19	—	—
15	II	80:20	—	16	—	—
16	II	70:30	105	—	—	—
17	II	50:50	130	—	—	—
18	III	70:30	65	52	1.46	6.06
19	III	50:50	77	44 *	2.17	3.74
20	III	30:70	114	48	1.4	1.8
21	IV	80:20	88	—	—	—
22	IV	60:40	105	—	—	—
23	V	70:30	82	54	—	—
24	V	50:50	118	50.8	—	—

* a minor transition was also noted at -9.7 deg.C

- Oxygen Permeability reported as (cc oxygen per mil thickness/100 sq.inches/day)

As the results of Table 5 illustrate, the inclusion of even minor amounts of the amorphous copolyamides (B) into blend compositions provided significant improvements in the "dry" glass transition temperatures, and in the examples shown, in the "wet" glass transition temperatures as well. Further, the reported values of oxygen permeability again as compared to the Comparative Example C1 illustrates a significant improvement in barrier properties under both "dry" and "wet" conditions.

It will be appreciated that the instant specifications and examples set forth herein are by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention, whose limitations are bounded only by the appendant claims.

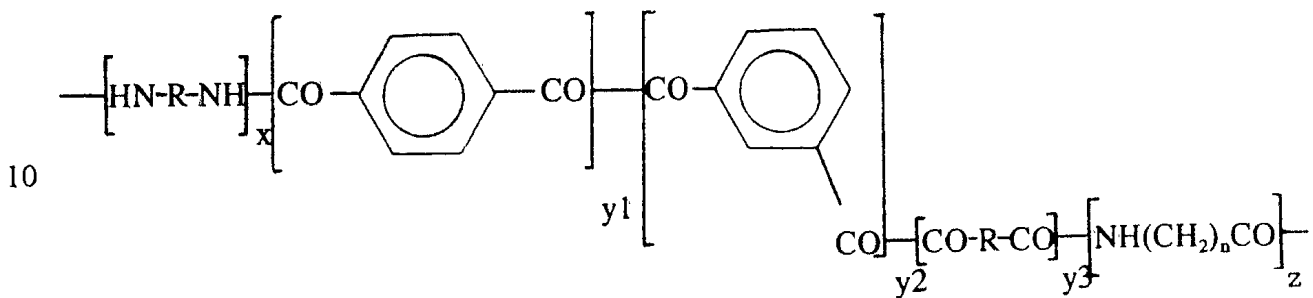
Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A thermoplastic polymeric composition comprising:

(A) a first polyamide which is one or more aliphatic or cycloaliphatic polyamides; and

5 (B) a second amorphous copolyamide which is represented by the following formula:



15

wherein:

$$x + y1 + y2 + y3 + z = 1$$

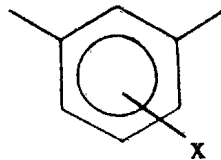
20

and,

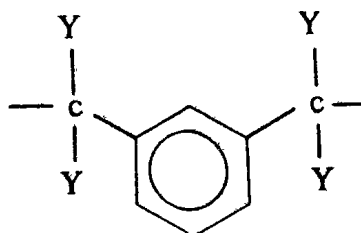
$$y1 + y2 + y3 = x$$

25

wherein n has a value of 5 - 11, and z = 0 - 0.5 and wherein R may be selected from the group consisting of :



35



wherein x is selected from the group consisting of $-\text{CH}_3$ -, an n-alkyl group, and halides, Y is selected from the group consisting of H and $-\text{CH}_3$ -, and R^1 is an α,ω -alkylene radical containing 4 to 18 carbon atoms wherein (A) and (B) are substantially miscible when formed into a blend composition.

- 5 2. A thermoplastic polymeric composition according to claim 1 wherein said composition comprises about 50-95% of polyamide A and about 5-50% of polyamide B.
3. A thermoplastic polymeric composition according to either of claims 1 or 2 wherein polyamide B has a T_G at least 100°C , measured at a relative humidity of less than 25%.
4. A thermoplastic polymeric composition according to any one of claims 1 to 3 wherein
10 polyamide B has a T_G of at least 25°C , measured at a relative humidity of 100%.
5. A thermoplastic polymeric composition according to any one of claims 1 to 4 wherein polyamide A is selected from the group consisting of polycaprolactam, polyhexamethylene adipamide, and copolymers thereof.
6. A thermoplastic polymeric composition according to any one of claims 1 to 5 wherein
15 a blend of said polyamide A and said amorphous polyamide B are sufficiently miscible such that said blend exhibits a single T_G .
7. A thermoplastic polymeric composition according to any one of claims 1 to 6 wherein Y is $-\text{CH}_3$.
8. A thermoplastic polymeric composition according to any one of claims 1 to 7 wherein
20 $n = 5$.
9. A film formed from a thermoplastic polymeric composition according to any one of claims 1 to 8.
10. A film formed from a thermoplastic polymeric composition according to any one of
25 claims 1 to 8 wherein said film has an oxygen permeability, measured at a relative humidity of greater than 90%, of less than or equal to 8.8cc of oxygen per mil thickness per 100 square inches per day.

11. A thermoplastic polymeric composition substantially as herein described with reference to the examples.

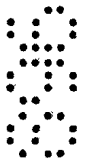
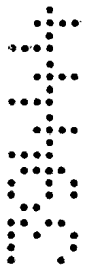
12. A film substantially as herein described with reference to the examples.

5 DATED this 29th DAY of July, 1996.

ALLIED-SIGNAL INC.

By its Patent Attorneys

DAVIES COLLISON CAVE



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/03093

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 Int. Cl. 5 C 08 L 77/02 C 08 L 77/06 //(C 08 L 77/02
 C 08 L 77:00) (C 08 L 77/06 C 08 L 77:00)

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int. Cl. 5	C 08 L

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US,A,4826955 (M.K. AKKAPEDDI) 2 May 1989, see whole document (cited in the application) -----	1
Y	EP,A,0475720 (MITSUBISHI) 18 March 1992, see examples; claims -----	1
Y	EP,A,0288972 (MITSUBISHI) 2 November 1988, see claim 8; page 5, lines 24-55 -----	1
Y	Patent Abstracts of Japan, vol. 016, no. 183 (C-0936), 6 May 1992, & JP,A,4023863 (KISHIMOTO) 28 January 1992 -----	1

⁹ Special categories of cited documents : ¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 13-07-1993	Date of Mailing of this International Search Report 0 5. 08. 93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer A. LEROY

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9303093
SA 72437

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 20/07/93. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		CA-A- 1301404	19-05-92
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		CA-A- 1279811	05-02-91
		US-A- 4908272	13-03-90